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Mildred A. Post, et al

Robert A. Taft Sanitary Engineering Center
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by

Mildred A. Post and W. Allan Mo[illegible]

Robert A. Taft Sanitary Engineering Center
U. S. Public Health Service
Cincinnati, Ohio

Approximately one hundred twenty water treatment plants in the United States and Canada (1, 2, 6) now use chlorine dioxide, usually in combination with chlorine, for sterilization purposes. Chlorine dioxide is also used for the control of tastes and odors caused by natural and industrial contaminants of water. These impurities include phenols, algae, actinomycetes, sewage, and decayed vegetation (15, 12, 9). Because of the high oxidation capacity of chlorine dioxide, metallic ions are readily converted in water to their insoluble oxides, which either settle out or are removed by sand filters (11, 13, 7).

Chlorine dioxide is also employed in the bleaching of flour, fats, and oils, of wood pulp for the paper industry, and in the bleaching and finishing of textiles (16, 4).

Current methods (14, 3, 10, 5) for the determination of chlorine dioxide either do not make a distinction between this compound and other forms of chlorine or are not sufficiently sensitive at low concentrations.

Because of the important uses for chlorine dioxide, coupled with the fact that no specific sensitive method exists for its determination, this investigation was undertaken.

EXPERIMENTAL

Study of Other Proposed Methods

The orthotolidine method[14] makes no distinction between chlorine and chlorine dioxide. It was established in this laboratory that chlorine can

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be eliminated by means of malonic acid and an attempt was made to use this reaction in adapting the orthotolidine method to chlorine dioxide. However, no definite relationship could be obtained between the color derived from known concentrations of chlorine dioxide and orthotolidine and the permanent chlorine standards recommended by Standard Methods.(14)

The OTA method employs sodium arsenite to distinguish between colors caused by chloramines, chlorine, and chlorine dioxide, and interfering ions. Here also, no differentiation was possible between chlorine and chlorine dioxide.

Another method(10) has been proposed to differentiate between chlorine and chlorine dioxide. This is the orthotolidine-arsenite-oxalic acid (OTO), an adaptation of the OTA test, in which oxalic acid is used to "tie up" the chlorine present. Numerous experiments were made employing this method. When a sample containing 1 ppm of chlorine was used a ten-minute contact time with oxalic acid eliminated color formation with orthotolidine, as claimed by the authors. It was also established that oxalic acid did not affect the color produced by chlorine dioxide with orthotolidine in concentrations as low as 0.05 ppm ClO_2. However, the OTO test could not be used for determining chlorine dioxide because of the lack of correlation, previously discussed, between OT color and chlorine dioxide concentration.

The amperometric method(14) employing phenyl arsenoxide was tried for both chlorine and chlorine dioxide. The results obtained for chlorine checked with the titration values very closely, but no positive results could be obtained for chlorine dioxide.

The tyrosine method described by Hodgden and Ingols(5) as specific for chlorine dioxide was investigated, but was found not to be sensitive at low concentrations.

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In an effort to obtain a more specific and sensitive indicator for chlorine dioxide, thirty different organic compounds were checked. Many of these were naphthol and amino naphthol sulfonic acids. Of these 1-Amino-8-Naphthol-3,6 Disulfonic Acid proved the most satisfactory. It is inexpensive, readily available, and can be easily purified.

Apparatus

Beckman Spectrophotometer Model B (5 cm. cells)

Beckman pH Meter

Assembly for generating chlorine dioxide. (Fig. 1)

Reagents

Chlorine Dioxide Solution

A chlorine dioxide solution free of chlorine was prepared by reacting C.P. sodium chlorite with 10% sulfuric acid, sweeping out the gas formed with air, and absorbing into 1500 ml. of distilled water. To determine whether a chlorine-free solution was generated by this procedure, the chlorine dioxide was dried by passing over calcium chloride and then over C.P. sodium chlorite to remove any chlorine that might possibly have been formed. Spectrophotometric readings showed that no appreciable difference in the purity of chlorine dioxide resulted from either of the two methods. The apparatus used is shown in Figure 1.

Ten grams of C.P. sodium chlorite is dissolved in 750 ml. of distilled water contained in a two-neck round bottom flask which is then connected to the receiver. Twenty ml. of 10% sulfuric acid is placed in the graduated cylinder fitted into the side neck of the flask and added in 5 ml. increments at five-minute intervals. Air agitation is started prior to the first addition and the cylinder is raised slightly at each addition. Air is bubbled through the solution for approximately 1/2 hour after the last acid

addition or until a deep yellow chlorine dioxide solution is obtained in the receiver. This should be stored in dark bottles away from light and prepared fresh weekly.

Standard Chlorine Dioxide Solution

This should be prepared fresh daily and stored in a tightly stoppered volumetric flask. Dilute 25 ml. of stock solution to two liters with distilled water and mix well. To 250 ml. of this solution in a 500 ml. erlenmeyer flask, add (by pipette) 10 ml. of 10% KI and 10 ml. of 10% H_2SO_4, stopper tightly, mix well and let stand in the dark for five minutes. Titrate the liberated iodine with N/40 sodium thiosulfate using starch solution as the indicator. The 250 ml. aliquot should require 5-8 ml. of N/40 sodium thiosulfate. If the solution is stronger than this, chlorine dioxide is easily lost.

In preparing a series of readings, no more than seven aliquots should be taken from one solution before redetermining its strength, since chlorine dioxide is very volatile. Replace the rubber stopper firmly after each withdrawal and keep in the dark when not in use.

Reaction: $2\ ClO_2 + 10\ HI \rightarrow 2\ HCl + 4\ H_2O + 5\ I_2$

$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$ (8)

Therefore $1\ ClO_2\ 5Na_2S_3O_3$

$Na_2S_2O_3\ \ \frac{ClO_2}{5}$

$$\text{Ppm } ClO_2 = \frac{\text{ml. N/40 } Na_2S_2O_3 \times .3375 \times 1000}{\text{volume of sample}}$$

Stock Chlorine Solution

A stock solution was prepared by bubbling chlorine gas slowly into distilled water. It was necessary to prepare this solution daily because an oily film formed on the surface with longer standing. Preparation of this solution should be carried out in diffused light; the solutions should be stored in dark bottles and kept in the dark.

Standard Chlorine Solution

A standard solution should be prepared fresh daily by diluting 10 ml. of stock solution to two liters with distilled water and mixing well. The same method for titration as that recommended for chlorine dioxide should be used, observing the same precautions.

$$\text{Ppm } Cl_2 = \frac{\text{ml. N/40 } Na_2S_2O_3 \times .886 \times 1000}{\text{volume of sample}}$$

1-Amino-8-Naphthol-3,6-Disulfonic Acid (H Acid)(Purification).

A good technical grade of H acid should be light gray in color. Dissolve 100 g. of the dry powder in 740 ml. of distilled water and add enough sodium carbonate to give a slight test to pink litmus. This requires approximately 22 g. Add 5 g. of Darco and 5 g. of Celite. Stir for ten minutes and filter by suction. Precipitate the H acid from solution with approximately 40 ml. of C.P. HCl to a definite blue test to congo red paper. Filter by suction using sharkskin filter paper and wash the filter cake with 100 ml. of distilled water. Press dry and repurify as above. H acid with a single purification gives a high blank so it is best to recrystallize twice. Dry the filter cake overnight in an oven at 60°C. Store in a dark bottle. The yield of dry powder is about 72 g.

Distilled Water

The distilled water used in making up all reagents and dilutions must be both chlorine and chlorine dioxide demand free. Such water was prepared according to Standard Methods.[14]

H Acid Solution

Dissolve 0.85 g. (.0025 mols) of the purified dry powder in 50 ml. of ethylene glycol (b 195-97) by heating slightly. When in solution add 50 ml. of water. A pale green solution is obtained which should be stable for one week at room temperature. If kept in a dark bottle at 20°C or lower, stability can be extended to two weeks.

An alternate preparation is to dissolve 0.85 g. of H acid in 100 ml. of distilled water in which it is more soluble than in ethylene glycol. However, this solution darkens quite readily and must be made fresh daily.

Sodium Acetate Buffer

Dissolve 243 g. of C.P. $CH_3COONa.3H_2O$ and 360 ml. of glacial acetic acid in water and dilute to one liter. The pH should be 4.1-4.3.

Malonic Acid Solution

Dissolve 1.0 g. of Malonic acid (Pract.) in water and dilute to one liter.

Ferric Chloride Solution

Dissolve 0.0484 g. of $FeCl_3.6H_2O$ in water and dilute to one liter. One ml. contains 0.01 mg. Fe.

Zinc Sulfate Solution

Dissolve 130 g. of $ZnSO_4.7H_2O$ in water and dilute to one liter.

Sodium Hydroxide

A 0.5 N solution is used.

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Sulfuric Acid

A 10% solution (by volume) is used. With this reagent demand-free water is not necessary.

PROCEDURE

Preparation of Standard Curve for Chlorine Dioxide

To a 100 ml. volumetric flask approximately half filled with chlorine dioxide demand-free water, pipette the required amount of chlorine dioxide standard solution below the surface of the liquid so that no loss will occur. Immediately close the flask with a glass stopper and keep closed until ready to complete the determination. A series of such solutions is prepared in the concentration range of 0.05 to 1.5 ppm ClO_2. Then add from a pipette 5 ml. of the acetate buffer. In adding reagents, avoid pipettes with very small tip openings. The reagents should be added as rapidly as possible in order to avoid loss of chlorine dioxide. Then add 1.0 cc of $FeCl_3$ solution and dilute to the mark with ClO_2 demand-free water. Following dilution, 0.4 ml. of the H acid reagent is added and the mixture shaken. Keep in the dark until ready to read.

Twenty to twenty-five minutes after shaking, determining the optical density at 525 mu against distilled water in the comparison cell (5 cm. cells are preferable). If desired, the time element can be longer but it should be consistent for all the samples and the same as that employed in making the standard curve. A blank is run using all of the reagents in the absence of chlorine dioxide. It is necessary to determine the blank correction daily.

A sufficient interval should be allowed between completion of each solution to avoid any difficulty in making the photometer readings on time.

The standard curve for chlorine dioxide is shown in Figure 3 and the reading at 525 mu is based on the absorption curve previously obtained (figure 2). From the standard curve it is noted that Beer's law is followed up to 1.5 ppm of chlorine dioxide.

Preparation of Standard Curve for Chlorine

Following exactly the same procedure as for chlorine dioxide, use chlorine demand-free water for samples and blank. The standard curve obtained for chlorine is given in Figure 4. Beer's law is shown to be followed up to a concentration of 1 ppm chlorine.

Determination of Chlorine Dioxide

If chlorine or chloramines are known to be absent, the following procedure is used. To a 100 ml. volumetric flask, add 90 ml. of sample. Then add 5 ml. of the acetate buffer, 1.0 ml. of ferric chloride solution and dilute to the mark with demand-free water. Following dilution add 0.4 ml. of H acid solution, mix well, and keep in the dark until the reading is taken. Run the blank and subtract from the reading. Net reading x 100/90 equals reading which would be obtained for undiluted sample. The concentration of ClO_2 is read from the standard curve.

Elimination of Chlorine Interference

In order to determine chlorine dioxide, in the presence of chlorine, a method first had to be found for eliminating chlorine interference. Investigation showed that 0.2 ml. of oxalic acid (saturated solution diluted 1:10) would eliminate 1 ppm of chlorine. However, it was impossible to obtain replicate absorbance readings on 0.05 ppm ClO_2 in the presence of this amount of oxalic acid. Another drawback to the use of oxalic acid was the formation of precipitates in hard water.

Malonic acid was tried and proved successful in eliminating chlorine. It was determined experimentally that 1 ppm of chlorine could be destroyed by 1 ml. of a 0.1% malonic acid solution in 0.5 hr. and 5 ppm Cl_2 by 2 ml. in twenty minutes. Two ml. of this solution did not affect the absorbance reading of 0.05 ppm ClO_2 nor did it form a precipitate in hard water. Five ml. of 0.1% malonic acid did definitely affect the reading for 0.05 ppm ClO_2.

Chlorine Dioxide in the Presence of Chlorine

To 90 ml. of sample in a 100 ml. volumetric flask, add 5 ml. of the acetate buffer, mix, add 2 ml. of 0.1% malonic acid and mix again. Stopper tightly and let stand in the dark for twenty minutes. Then add 1.0 ml. of ferric chloride solution and dilute to the mark with demand-free water. Add 0.4 ml. of H acid solution, shake well and keep in the dark until the reading is taken. The concentration of ClO_2 is read from the standard curve.

Chlorine

To obtain the concentration of chlorine present, repeat the above procedure omitting malonic acid. The absorbance reading obtained represents chlorine and chlorine dioxide. Subtract the chlorine dioxide reading obtained in the malonic acid procedure to obtain the value for chlorine.

Chlorine reading x 100/90 equals the reading for the undiluted sample. Read the concentration of chlorine from the standard curve which is given in Figure 3. Table 1 represents a check on this method.

Chlorine Dioxide in Water Containing Suspended Matter

To 90 ml. of sample in a graduated separatory funnel, add 1.0 ml. of zinc sulfate solution and 1.7 ml. of 0.5 N NaOH. Dilute to the 100 ml. mark with demand-free water. Close with glass stopper, mix, and allow the

floc to settle. Draw off to the 80 ml. mark and then run the clear supernatant into a 100 ml. volumetric flask. Add 5 ml. of the acetate buffer, mix, and eliminate the chlorine present by the addition of 2.0 ml. of 0.1% malonic acid and allow to stand twenty minutes. If chlorine is known to be absent, this step can be omitted. Then add 1 ml. of ferric chloride solution and, following dilution to 100 ml., add 0.4 ml. of H acid reagent. Shake well and let stand in the dark for twenty minutes, and then determine the absorbance at 525 mu.

90/100 x 80 = 72 ml. = actual volume of sample used

100/72 x net reading = absorbance for undiluted sample

Some loss of chlorine dioxide will occur with this method. There is absorption by the floc and loss of ClO_2 when the supernatant liquid is transferred from the separatory funnel to the flask. A solution containing 0.3 ppm ClO_2, when treated in the manner, gave a final concentration of 0.25 ppm.

Chlorine dioxide may be determined visually by preparing a series of standards in the range of 0.05 to 1.0 ppm. With higher concentrations of ClO_2 the color is too intense to be read visually.

FACTORS AFFECTING THE DETERMINATION

Effect of Heat

Since the strength of chlorine and chlorine dioxide solutions is easily affected by heat, it is advisable to carry out all determinations at a room temperature of 20-25°C.

Effect of Reagent Concentration

No increase in color could be obtained by the addition of more than 0.4 ml. of H acid reagent.

Effect of pH

It was determined experimentally that a pH of 4.1-4.3 was the best workable range for determining chlorine dioxide. In this pH range maximum absorption can be obtained using an acetate buffer. This buffer has the added advantage of easily controlling the pH of hard water. The use of potassium acid phthalate buffers was found to be unsatisfactory in the presence of iron.

Chloramines are unstable at pH 4.1-4.3 and the chlorine, formed from their decomposition, can be destroyed with malonic acid.

Function of Ferric Chloride

The purpose of adding ferric chloride is to increase the sensitivity of the reaction. In addition to deepening the color especially for the low concentrations of chlorine dioxide, it appears to have a stabilizing influence; it is much easier to obtain replicate readings when it is used. It is well known in dyestuff chemistry[17] that some metallized dyes are superior in stability and fastness to light in comparison with dyes of the same composition where the metal is omitted. The same type of stability may be the factor involved here.

Interferences

Table 1 shows the effect of ferric, cupric, and manganous ions on the determination of chlorine dioxide. The presence of iron and copper to 0.5 ppm and of manganese to 0.2 ppm does not effect a significant change in results. In view of the fact that chlorine dioxide converts these metals to their insoluble oxides, it would seem unlikely that concentrations greater than those mentioned would be found in a treated water supply. Chlorine dioxide has been found superior to chlorine in the oxidation of manganese[13].

Table 3 shows the influence of diverse ions on the determination of chlorine dioxide. The concentrations given for most of the ions are reasonably close to those occurring in treated waters. Nitrites in concentrations greater than 0.5 ppm will show a positive interference. Should nitrites in higher concentrations be present, they can be destroyed in ten minutes, by first adding to the neutralized samples 0.45 ml. of 10% H_2SO_4 and 1 ml. of 1% sulfanic acid.

Of all the ions studied polyphosphates show the greatest interference. At the present time we have been unable to determine the exact mechanism of this interference or to eliminate it. In those water treatment plants which use polyphosphates routinely in the treatment process it will be necessary to make the standard curve in the presence of the concentration known to be present.

RECOVERY OF CHLORINE DIOXIDE IN VARIOUS TYPES OF WATERS

In order to test the practicability of the proposed method for chlorine dioxide, known amounts of this compound were added to various types of waters, made demand-free, and the concentrations then determined. The deep well water used contained approximately 400 ppm total hardness. The results tabulated in Table 4, show close correlation between the concentrations of chlorine dioxide added and found, and indicate that the procedure given for determining chlorine dioxide is a practical method well adapted to different types of waters.

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It should be pointed out that this procedure does not distinguish between chlorites and chlorine dioxide. Chlorites at pH 4.2 will decompose with the formation of chlorine dioxide which will also be measured colorimetrically. If, however, only chlorine dioxide is applied in water treatment plants, there will be no problem of chlorite interference. At one

water plant where chlorine dioxide is generated by passing chlorine gas into a sodium chlorite solution, the pH of this reaction mixture was 3, at which the chlorite would decompose to chlorine dioxide.

SUMMARY

Chlorine dioxide may be determined in a treated water supply by reacting with 1-Amino-8-Naphthol-3,6-Disulfonic acid and measuring the bluish-pink color produced by means of the Beckman B spectrophotometer at 525 mu. This reaction is carried out in an acetate buffered solution at a pH of 4.1-4.3. Reliable determinations can be made in the range of 0.05 ppm to 1.5 ppm and between these concentrations Beer's law is followed. Visually, 0.05 to 1.0 ppm ClO_2 can be determined. Chlorine interference up to 5 ppm Cl_2 can be eliminated by means of malonic acid. The effect of interfering ions-nitrites, ferric, cupric, and manganous ions is discussed and procedures given for their elimination when necessary. By obtaining a total reading on chlorine dioxide and chlorine and then eliminating chlorine, the concentration of ClO_2 can be determined by difference. Since chloramines are not stable at pH 4.2, the chlorine measured is derived also from chloramines.

Table 1 - Determination of Chlorine Dioxide And Chlorine in a Mixed Solution

Added, Mg/l		Found, Mg/l	
ClO_2	Cl_2	ClO_2	Cl_2
0.05	1.0	0.05	1.0
0.1	0.1	0.1	0.1
0.1	0.5	0.1	0.5
0.5	0.1	0.5	0.1

Table II - Effect of Metals on Determination of ClO_2

ClO_2 added	Metal added	ClO_2 Found, mg/l		
mg/l	mg/l	Mn	Fe	Cu
0.30	0.00	0.29	0.28	0.28
"	0.01	0.29	-	-
"	0.07	0.29	-	-
"	0.10	0.30	0.28	0.31
"	0.20	-	0.29	0.31
"	0.30	-	0.30	0.31
"	0.40	-	0.31	0.30
"	0.50	-	0.32	0.30

Table III - Effect of Diverse Ions
On the Determination of ClO_2*

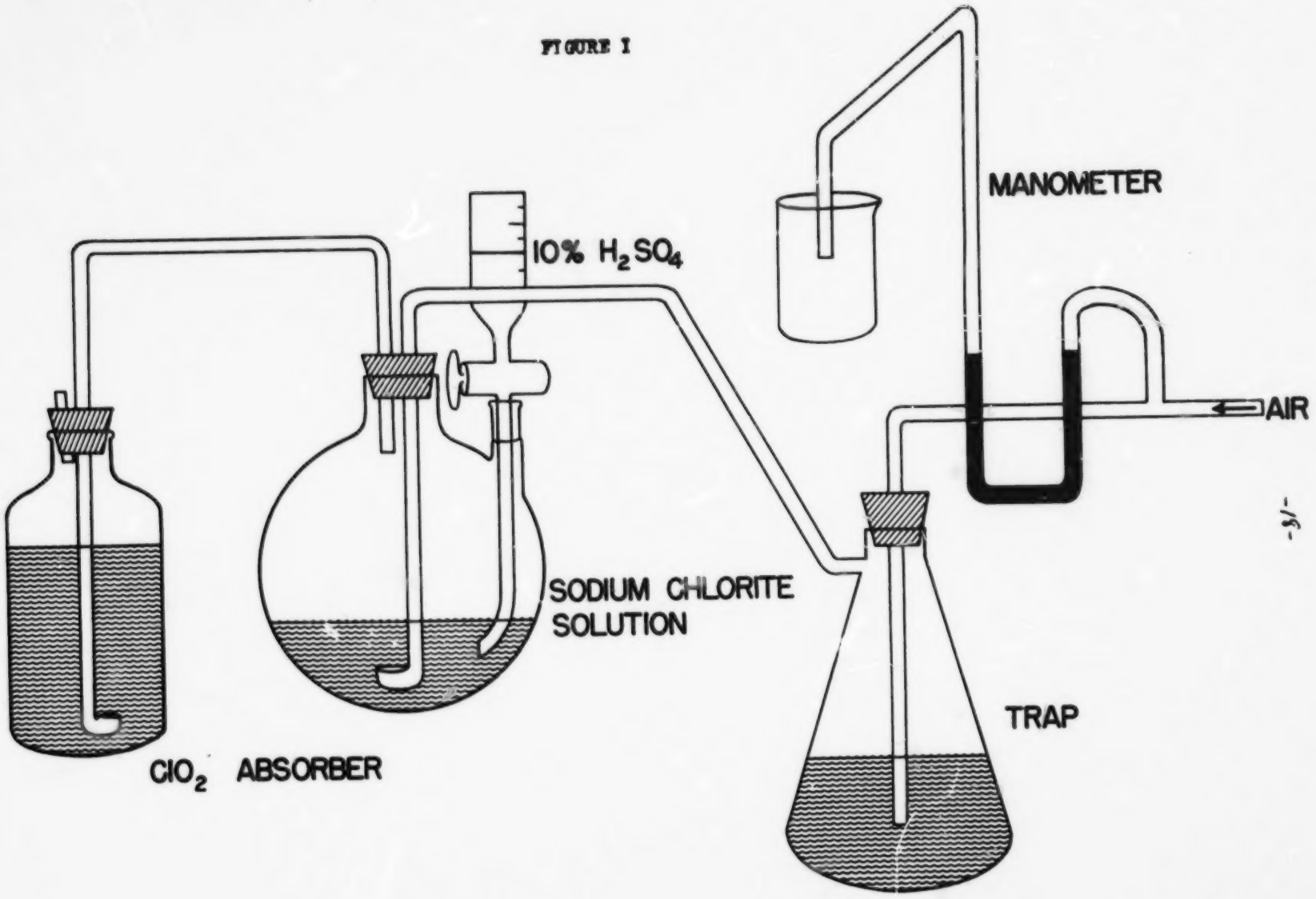
Ion added	Concentration of Ion Added, mg/l	Concentration of ClO_2 Found, mg/l
NH_4^+	0.2	0.20
Na^+	500	0.20
Ca^{++}	100	0.20
Mg^{++}	100	0.20
Al^{+++}	0.1	0.20
Zn^{++}	200	0.20
Pb^{++}	0.05	0.19
Cl^-	300	0.20
ClO_3^-	5.0	0.20
$PO_4^{\equiv}$(ortho)	0.1	0.20
$PO_4^{\equiv}$(pyro)	1.0	0.15
$PO_4^{\equiv}$(hexameta)	0.5	0.17
$PO_4^{\equiv}$(hexameta)	1.0	0.13
$SO_4^{\equiv}$	600	0.20
NO_3^-	10.	0.20
F^-	6.	0.20
NO_2^-	0.5	0.22
$SiO_3^{\equiv}$	0.2	0.19

+ 0.20 mg/l ClO_2 added

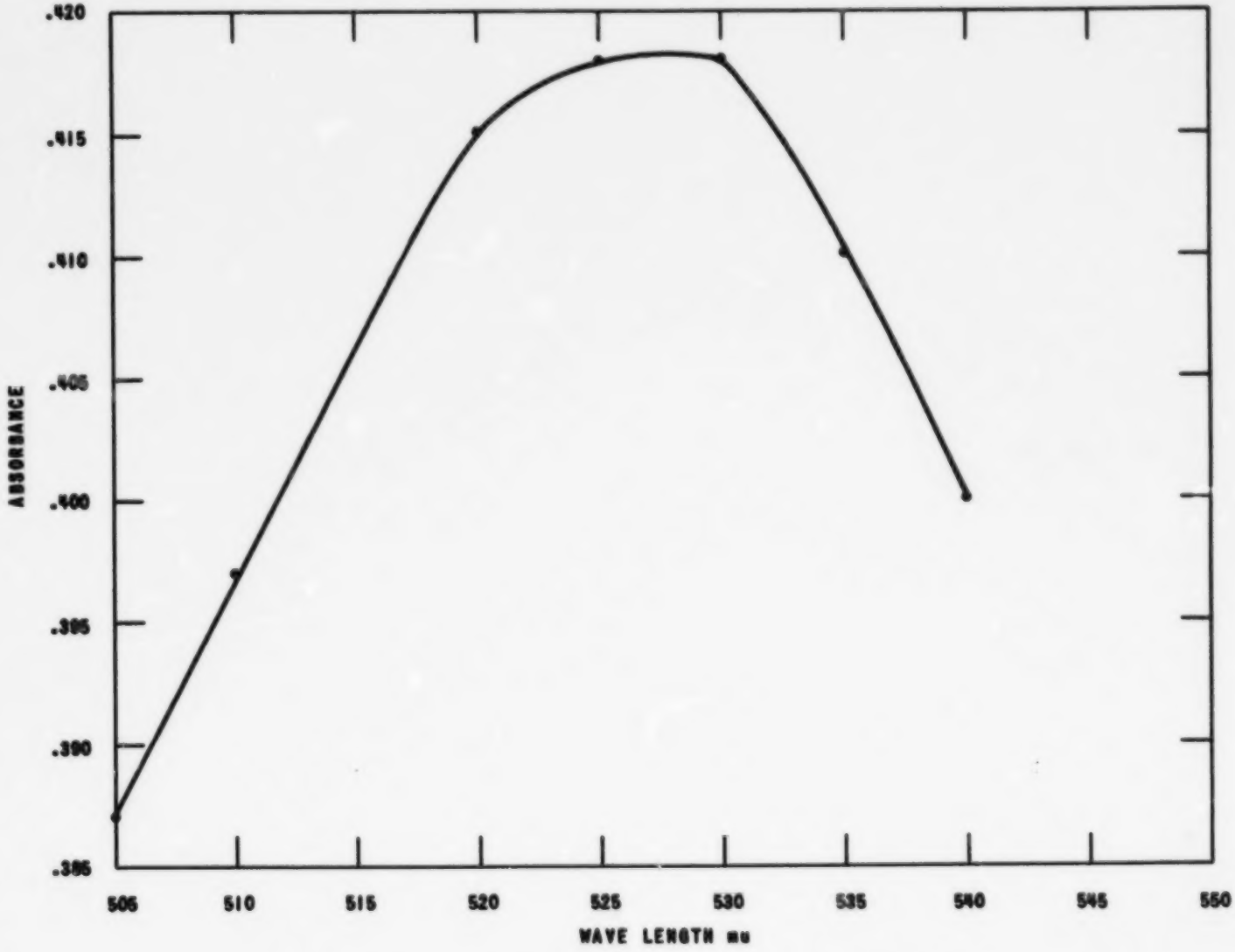
Table IV- Determination of ClO_2 in Various Types of Water

ClO_2 added mg/l	ClO_2 Found, ppm mg/l		
	Tap Water	Well Water	River Water
0.05	0.047	0.047	0.047
0.10	0.10	0.10	0.10
0.30	0.30	0.31	0.29
0.50	0.50	0.52	0.49
0.60	0.59	0.61	0.58
0.80	0.79	0.82	0.78
1.00	0.99	1.00	0.98

FIGURE I

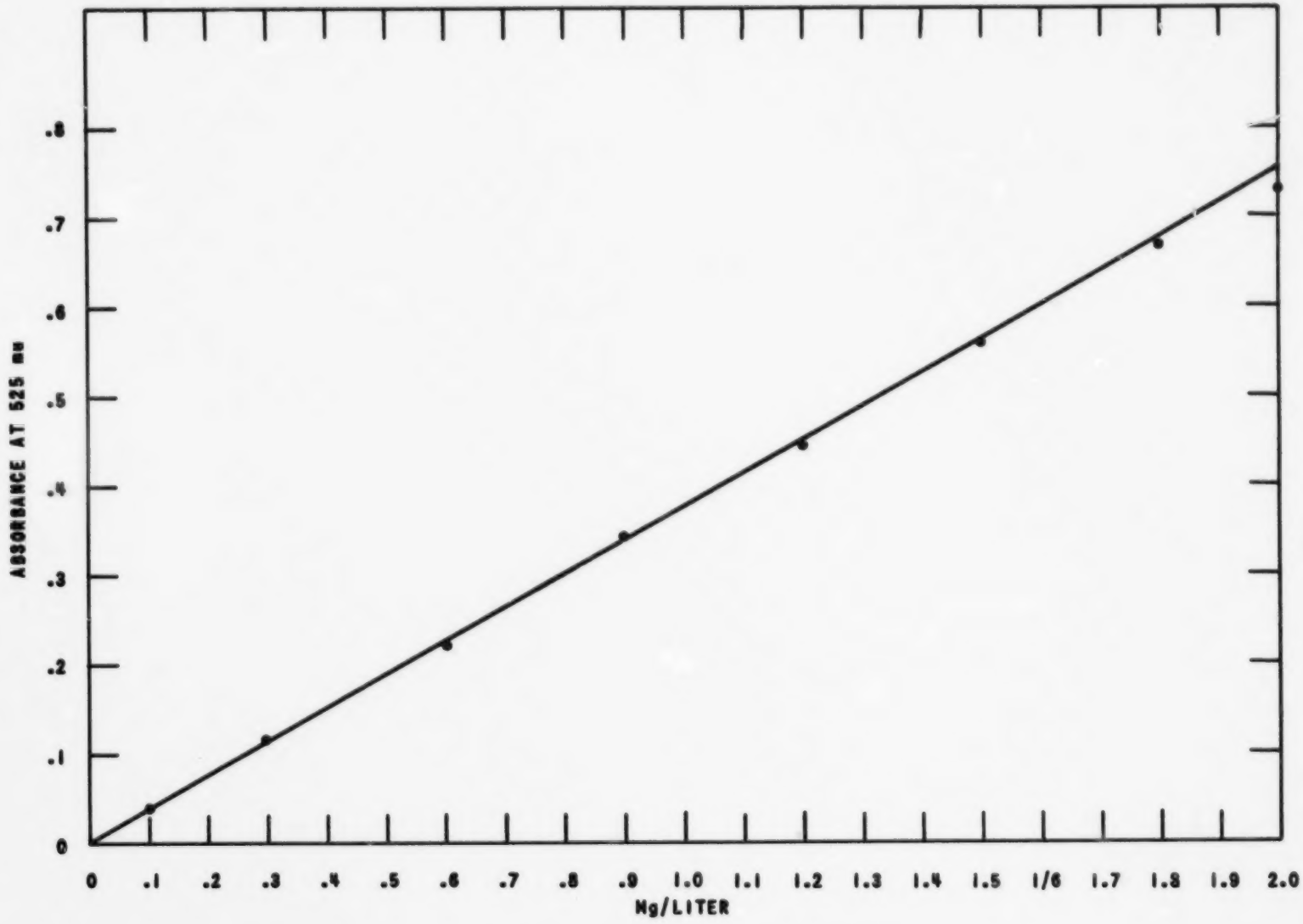


CHLORINE DIOXIDE GENERATOR



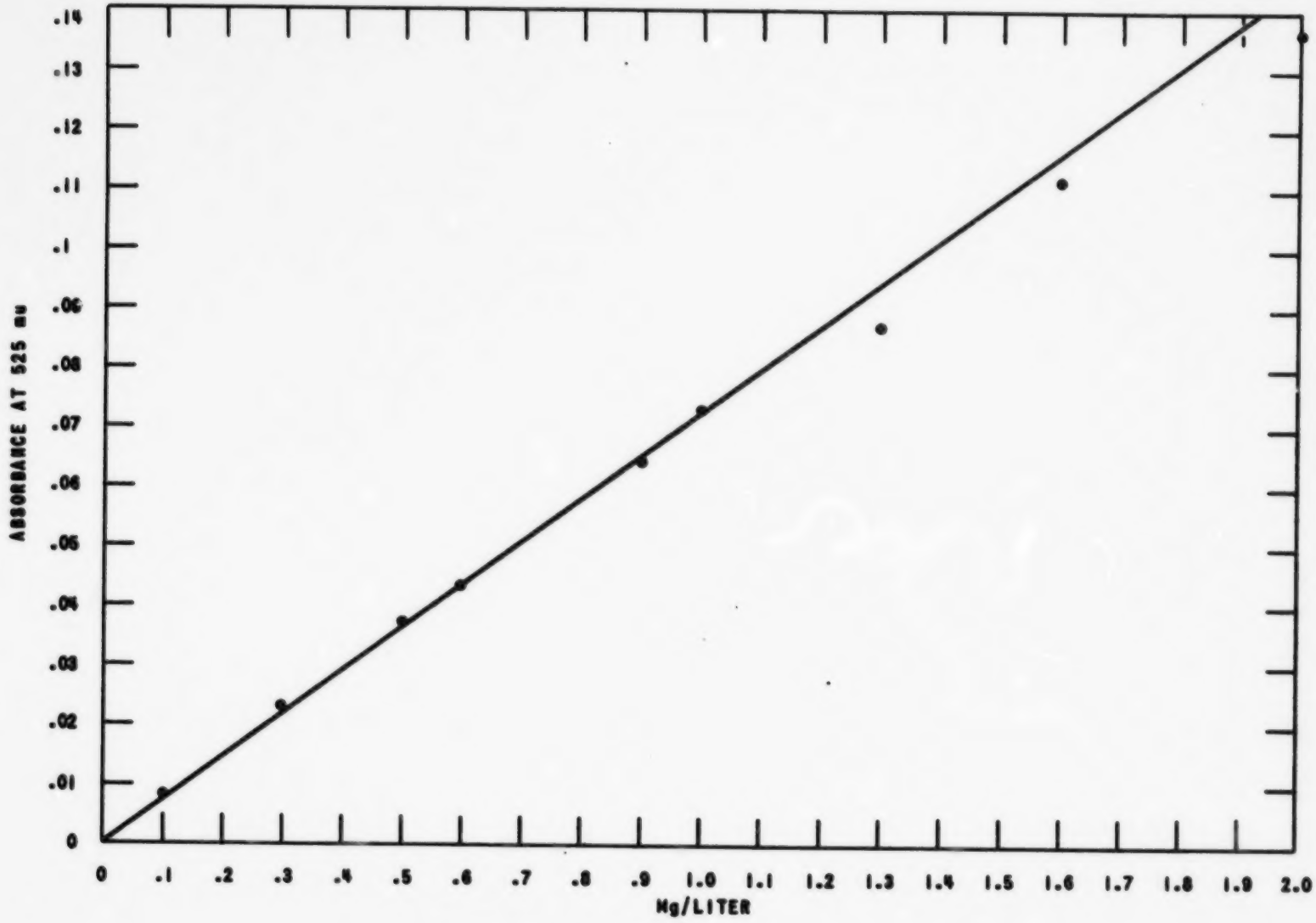
ABSORPTION CURVE FOR CHLORINE DIOXIDE - H ACID

Figure II



STANDARD CURVE FOR CHLORINE DIOXIDE

Figure III



STANDARD CURVE FOR CHLORINE

Figure IX

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